



# The effects of 1-MCP treatment on fruit quality of medlar fruit (*Mespilus germanica* L. cv. Istanbul) during long term storage in the palliflex storage system



Nurten Selcuk, Mustafa Erkan\*

Department of Horticulture, Faculty of Agriculture, Akdeniz University, 07059 Antalya, Turkey

## ARTICLE INFO

### Article history:

Received 7 July 2014

Received in revised form

10 September 2014

Accepted 19 September 2014

Available online 10 October 2014

### Keywords:

Medlar fruit (*Mespilus germanica* L.)

1-Methylcyclopropene

Palliflex storage system

Antioxidant activity

Fruit quality

## ABSTRACT

In this study, the effects of 1-methylcyclopropene (1-MCP) treatments on ripening properties, postharvest characters, antioxidant activity, organic acids and sugar contents in medlar (*Mespilus germanica* L. cv. Istanbul) fruit were investigated. Medlar fruit were harvested at commercial harvest maturity and treated with 0.2, 0.4 and 0.6  $\mu\text{L L}^{-1}$  of 1-MCP for 24 h at  $0 \pm 0.5^\circ\text{C}$  in a hermetically sealed 100 L containers, and stored under the palliflex storage system (21%  $\text{O}_2 + 0.03\% \text{CO}_2$ ) at  $0 \pm 0.5^\circ\text{C}$  temperature with  $90 \pm 5\% \text{RH}$  for 60 days. Most of the physiological and biochemical changes during storage and ripening were affected by 1-MCP in a dose-dependent manner. The two higher concentrations 1-MCP treatments extended the storage life, decreased weight loss and delayed the rate of softening, loss of taste, browning incidence in skin color ( $C^*$  and  $h^\circ$  values). 1-MCP treatments also retarded the decline of titratable acidity. During the early stage of storage, total phenolics, total flavonoids, total condensed tannins, ascorbic acid, antioxidant activity and organic acids gradually decreased in all treatments. The reduced changes in the total phenolics, total flavonoids, total condensed tannins, ascorbic acid, antioxidant activity, as well as individual organic acid (malic and oxalic acids) contents showed the effectiveness of 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP in retarding fruit ripening. These results demonstrate that 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treatments were effective in extending postharvest life and maintaining the quality of medlar fruit.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Medlar (*Mespilus germanica* L.) is a member of the Rosaceae family and is native to southeastern Europe, Anatolia, Crimea, Caucasasia and the northern parts of Iraq and Iran. The medlar fruit is brown, sometimes reddish tinged, pear and apple shaped fruit ranging from 1.5 to 3 cm in diameter and weighing from very small (about 10 g) to large (more than 80 g) (Browicz, 1972). The fruit is hard when ripe, and they become brown, soft, sweet and edible after harvesting (Dirr, 1990).

The medlar fruit has gained in popularity in human consumption and commercial importance in recent years. Medlar fruit is a rich source of health promoting phytochemicals including antioxidants, such as phenolics, flavonoids, ascorbic acid and tannins (Ayaz et al., 2008; Rop et al., 2011; Gruz et al., 2011; Gulcin et al., 2011; Nabavi et al., 2011; Selcuk and Erkan, 2015).

The medlar fruit is widely grown and consumed in Turkey, and in northeast Anatolia (Turkey), both wild and cultivated forms are grown, and their fruit is used in different ways. The astringency of the fruit is well known and it has been reported that pulp or syrup of the ripened fruit was a popular remedy against enteritis and has many human healing properties. The medlar fruit is also used as treatment of constipation, as a diuretic and to rid the kidney and bladder of stones (Baytop, 1999). Medlar fruit are harvested through October and November in the northern hemisphere. In October, the hard fruit is harvested and stored in cold, dark and ventilated places. However, a substantial part of the crop at different stages of maturity is left on the trees, and is harvested later after fruit softening has started. The fruit is often consumed or sold in the local markets and stores. Medlar fruit show a typical climacteric ripening behavior (Ayaz et al., 2002; Selcuk and Erkan, 2015) and their quality properties change sharply after harvest. As in other climacteric species, ripening triggers softening and results in an increase in total soluble solids content and a decrease in titratable acidity. Medlar fruit is highly perishable and susceptible to skin and flesh browning, fast softening and water loss after harvest, which greatly affects its edible and commercial value. Generally,

\* Corresponding author. Tel.: +90 242 310 2428; fax: +90 242 310 4564.  
E-mail address: [erkan@akdeniz.edu.tr](mailto:erkan@akdeniz.edu.tr) (M. Erkan).

the fruit quality markedly decreases at room temperature for about 3–5 days after harvest. Reduction of fast softening should therefore be avoided during postharvest handling and storage to protect fruit quality and increase postharvest life. To limit these problems, medlars are handled and stored at cold temperatures by using different storage methods such as the palliflex storage system (Selcuk and Erkan, 2015).

The palliflex storage system is suitable for short and long term storage under CA and ultra low oxygen (ULO) conditions. In this storage system, it is possible to set desired  $O_2$  and  $CO_2$  compositions in individual pallets by creating CA conditions.  $O_2$  and  $CO_2$  can be automatically injected or removed, based on operator set points programmed into the controller. This system is suitable for different fruit and vegetables in the same storage room, because it can provide different atmosphere compositions for individual pallets. The palliflex storage system is similar to CA and extends the useful marketing period of fresh produce during storage, transportation, and distribution by maintaining quality, nutrition, and market value of the produce beyond that achieved via the use of cold storage alone (Dogan and Erkan, 2014). In addition, the palliflex storage system has been shown to retard the degradation of bioactive compounds. Selcuk and Erkan (2015) reported that medlar can be benefitted by 2%  $O_2$  with 5%  $CO_2$  atmospheres in palliflex storage at a temperature of 0 °C, extending its postharvest life.

1-Methylcyclopropene (1-MCP) inhibits ethylene action and prevents ethylene-dependent responses such as softening and senescence of vegetables and fruit tissues (Sisler and Serek, 1997). 1-MCP, a strong blocker of ethylene receptors, is being used as a tool to further investigate the role of ethylene in ripening and senescence, and as a potential commercial tool to maintain product quality (Blankenship and Dole, 2003; Watkins, 2006). 1-MCP has been shown to reduce ethylene production and to delay softening in many fruit, such as apple, apricot, plum, avocado, peach, nectarine and pear (Watkins et al., 2000; Watkins, 2006). In the present study, 1-MCP was used to understand the softening and browning process occurring in medlar fruit during long term storage. 1-MCP has been extensively used on fruit at the experimental level in order to understand the mechanisms controlling the physiology and biochemistry of the ripening processes, and the effect of 1-MCP in delaying ripening has been studied on fruit including guava (Singh and Pal, 2008), apple (Fawbush et al., 2009), cherimoya (Li et al., 2009), pear (Li et al., 2013), mangosteen (Piriyavinit et al., 2011), plum (Singh and Singh, 2012; Minas et al., 2013), avocado (Zhang et al., 2011), litchi (Sivakumar and Korsten, 2010), high bush blueberry (Chiabrando and Giacalone, 2011) and jujube (Zhang et al., 2012). These data indicate that 1-MCP has potential for the commercial control of ripening and softening of different harvested horticultural crops. However, to the best of our knowledge, there is no information available on the effects of 1-MCP treatment on the storage of medlar fruit showing climacteric ripening behavior. In this study, we aim to investigate the effect of 1-MCP treatment of the medlar fruit on their postharvest characters such as visual quality, physiological and biochemical parameters in the palliflex storage system at 0 °C, and to provide information that might lead to a longer storage life for this short-lived crop.

## 2. Materials and methods

### 2.1. Fruit material

Medlar fruit (*Mespilus germanica* L. cv. Istanbul) were harvested from a commercial orchard in Egridir, Turkey, at the commercial maturity stage [total soluble solids (TSS) = 15.17%; total titratable acidity (TA) = 1.13%; firmness = 14.70 N] in the end of October. After harvest, medlars were immediately transported within 2 h via a

refrigerated truck to the postharvest laboratory and cold storage facilities of the Department of Horticulture at Akdeniz University (Antalya, Turkey). Fruit were selected for uniformity of shape, color and size, and any blemished or diseased fruit were discarded.

### 2.2. 1-MCP treatments and storage conditions

SmartFresh™ (1-MCP 0.14%) was supplied by AgroFresh Inc. (Rohm and Haas Inc., Turkey). Different amounts of the powder were weighed and distilled water was added to obtain doses of 0.2, 0.4 and 0.6  $\mu\text{L L}^{-1}$ .

Fruit were replaced into polypropylene plastic punnets (10 cm × 20 cm) and punnetted fruit (forty fruit per punnet) were separated into four groups with three replicates. Each set of three replicates was given one of four treatments: (1) control fruit (0  $\mu\text{L L}^{-1}$  1-MCP), (2) 0.2  $\mu\text{L L}^{-1}$  1-MCP, (3) 0.4  $\mu\text{L L}^{-1}$  1-MCP, and (4) 0.6  $\mu\text{L L}^{-1}$  1-MCP, applied for 24 h at 0 ± 0.5 °C in a hermetically sealed 100 L container. After 1-MCP treatment, treated and untreated (control) fruit were stored in the palliflex storage system (21%  $O_2$  + 0.03%  $CO_2$ ) at 0 ± 0.5 °C temperature with 90 ± 5% RH for 60 days.  $O_2$  and  $CO_2$  levels in the palliflex were established by a flow-through system and maintained at 21%  $O_2$  + 0.03%  $CO_2$  set level during the entire storage period. Fruit were evaluated on 0, 15, 30, 45, and 60 days of cold storage. For each evaluation, three punnets ( $n = 120$ ; forty fruit per punnet) from each treatment were processed. Fruit behavior during storage was assessed on the basis of weight loss, taste, fruit firmness, browning index, skin color, titratable acidity, total soluble solids, total phenolics, total flavonoids, total condensed tannins, ascorbic acid, antioxidant activity, organic acids and sugars.

### 2.3. Weight loss

Weight loss was determined by weighing the punnets at the beginning of the experiment (day 0) and at 15 day intervals. Cumulative weight loss was expressed as percentage loss of the initial total weight.

### 2.4. Taste analysis

Medlar fruit is very hard, astringent, and not edible at harvest and during the first 15 days of storage. So, taste analysis was assessed in fruit taken out of storage after 30, 45 and 60 days. Fruit were equilibrated to 20 °C before sampling. A taste panel of five experts trained evaluators used a scale of 1–5, where 1 indicates extremely low taste and 5, extremely good taste 1 = very poor; 2 = poor (limit of acceptable taste); 3 = good; 4 = very good; 5 = excellent. Scores of 3 or above were considered acceptable for commercial purposes.

### 2.5. Firmness

Flesh firmness was measured using a hand-held penetrometer (Digital Force Gauge, Chatillon 20755, Florida, USA) equipped with a conical probe (12 mm in diameter), measuring the peeled equatorial surface on 3 sides of the fruit. The results were expressed as newtons. For each test, 40 fruit with 3 replications were used.

### 2.6. Decay incidence

Fruit decay was visually evaluated during the experiment. Any medlars with visible mold growth were considered decayed. Decay was expressed as a percentage of total fruit.

## 2.7. Measurement of external browning index

Fruit browning was determined in 40 fruit with 3 replications. General appearance was estimated by measuring the extent of the browned area on fruit skin. The external browning index (EBI) was rated as 1 = none (excellent quality); 2 = slight (browning area <5%); 3 = moderate (browning area 5–25%); 4 = moderately severe (browning area 25–50%); 5 = extreme (browning area >50%). The EBI was calculated as  $\Sigma\{(\text{browning rating}) \times (\text{number of fruit with the browning rating})\} / (\text{total number of fruit in the sample})$  (Yang et al., 2010).

## 2.8. Skin color

External skin color (three measurements at three equidistant points on the equatorial region of each individual fruit) was measured on 40 fruit from each replicate using a color meter (CR 200, Minolta, Ramsey, NJ, USA) and recording CIE  $L^*$ ,  $a^*$ , and  $b^*$  values. Negative  $a^*$  values indicate green and positive  $a^*$  values red color. Higher positive  $b^*$  values indicate a more yellow skin color and negative  $b^*$  blue color. These values were then used to calculate hue angle, where  $0^\circ$  = red-purple;  $90^\circ$  = yellow;  $180^\circ$  = bluish green; and  $270^\circ$  = blue (McGuire, 1992), and Chroma, which indicates the intensity or color saturation.

## 2.9. Titratable acidity, and total soluble solids

Twenty grams of flesh tissue from the forty fruit per replicate were homogenized in 80 mL of distilled water. The homogenates were centrifuged at  $20,000 \times g$  for 20 min at  $30^\circ\text{C}$ . A 10 mL aliquot of supernatant was diluted with 30 mL of distilled water. The pH value was determined using a pH meter (720 WTW, Inolab, Weilheim, Germany) with a glass electrode. Titratable acidity (TA) was determined by titrating 10 mL of supernatant in 30 mL of distilled water with NaOH 0.1 N to an end point of pH 8.1 and expressed as a percent of citric acid equivalents. Total soluble solids (TSS) were measured by a digital refractometer (Model Number REF121, Atago, China) and expressed as percent.

## 2.10. Total phenolic contents, total flavonoid contents, total condensed tannin contents and determination of antioxidant activity using DPPH assay

Medlar fruit were stored at  $-20^\circ\text{C}$  until analyzed. Total phenolics, total flavonoids, total condensed tannins and antioxidant activity in the frozen fruit were extracted according to the methods of Zheng et al. (2003) with slight modifications. To prepare the fruit extracts, forty medlars from frozen samples from each replicate were cut into small slices, mixed. Three 5 g samples from each replicate were extracted with 50 mL of 80% acetone containing 0.2% formic acid using a homogenizer (Heidolph Silent Crusher M Homogenizer P/N-595-06000-00, Germany) for 2 min and then centrifuged at  $20,000 \times g$  for 20 min at  $4^\circ\text{C}$ . The supernatant was used for analysis of total phenolics, total flavonoids, total condensed tannins and antioxidant activity.

The total phenolic analyses were performed using the method described by Spanos and Wrolstad (1990). For this purpose, 100  $\mu\text{L}$  of the sample extract, 900  $\mu\text{L}$  of nanopure water, and 5 mL of 0.2 N Folin-Ciocalteu reagent were added to a 15 mL volumetric flask. The contents were mixed and allowed to stand for 5 min at room temperature. Next, 4 mL of saturated sodium carbonate ( $75\text{ g L}^{-1}$ ) was added. Solutions were mixed and allowed to stand at room temperature for 2 h. The absorbance of the final solution was recorded with a spectrophotometer (Analytic Jena UV-Vis L 40, Germany) at 765 nm wavelength against the blank solution (80%

aqueous acetone). The results were expressed as mg of gallic acid equivalent per 100 g of fresh weight (mg GAE  $100\text{ g}^{-1}\text{ fw}$ ).

Total flavonoid contents of the medlars extracts were determined using a colorimetric method described by Chang et al. (2006). 500  $\mu\text{L}$  of diluted fruit extract was mixed with 2.5 mL of distilled water. At zero time, 150  $\mu\text{L}$  of (5% w/v)  $\text{NaNO}_2$  was added. After 5 min, 300  $\mu\text{L}$  of (10% w/v)  $\text{AlCl}_3$  was added. At 6 min, 1 mL of 1 M solution of NaOH were added, and the final volume was made up to 5 mL with distilled water. The mixture was shaken vigorously and the absorbance was measured at 510 nm against a prepared blank solution (80% aqueous acetone). The results were expressed as mg of (+)-catechin equivalent per 100 g of fresh weight (mg CE  $100\text{ g}^{-1}\text{ fw}$ ).

For the determination of total condensed tannins, the vanillin-HCl method described by Broadhurst and Jones (1978) was adapted. Briefly, 0.5 mL of the extract was added to 3 mL of vanillin reagent (4%, w/v, vanillin in methanol) and mixed thoroughly. To this mixture 1.5 mL concentrated hydrochloric acid was added and vortex mixed. The solution was kept in the dark for 15 min at room temperature and the absorbance was read at 500 nm. A blank sample was prepared using the same procedure, but replacing the 0.5 mL of extract with the solvent used in extraction. The results were expressed as mg of (+)-catechin equivalent per 100 g of fresh weight (mg CE  $100\text{ g}^{-1}\text{ fw}$ ).

The antioxidant activity of the samples was analyzed by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay according to the procedures of Gadow et al. (1997) and Maisuthisakul et al. (2007). A 100  $\mu\text{L}$  aliquot of the diluted sample extract (prepared at 5 different concentrations to achieve 10–90% inhibition of DPPH radical) was added to 4 mL of freshly prepared DPPH (2,2-diphenyl-1-picrylhydrazyl radical) solutions ( $6 \times 10^{-5}\text{ M}$  in MeOH). The mixtures were shaken and kept in the dark at room temperature for 30 min. Absorbance values were recorded at 515 nm with respect to control solution (80% MeOH instead extract in DPPH solution). The antioxidant activity of the samples was expressed as percentage inhibition of the DPPH radical which was calculated by using the following Eq. (1):

$$I(\%) = \left[ \frac{(A_c - A_s)}{A_c} \right] \times 100 \quad (1)$$

where  $I$  is the inhibition percentage,  $A_c$  and  $A_s$  are the absorbance values of the control and test samples, respectively.

The sample extract concentration providing 50% inhibition ( $\text{EC}_{50}$ ) of the DPPH radical was calculated by plotting the concentration versus inhibition percentage (%). Using the same procedure,  $\text{EC}_{50}$  value of Trolox solution was also determined to compare antioxidant activity of the samples. Antioxidant activity of samples was also expressed as Trolox equivalent antioxidant capacity (TEAC).

## 2.11. Extraction and HPLC analysis of ascorbic acid, organic acids and sugars

An Agilent 1100 series HPLC system integrated with an autosampler (G1313A), including temperature control for the column (G1316A), a degasser system (G1379A), a quaternary gradient pump (G1311A), a photodiode-array detector (G1315B), a refractive index detector (1200 series), and a software package for system control and data acquisition (Agilent Chemstation software) were used for analyses.

Ascorbic acid (vitamin C) was extracted from the medlars following a modified method of Karhan et al. (2004). Fruit were stoned and homogenized for 1 min at medium speed in a manual blender. The homogenate (20 g) was added to 60 mL of 6% metaphosphoric acid with a homogenizer (Heidolph Silent Crusher M Homogenizer P/N-595-06000-00, Germany) at medium speed



for 1 min. Extracts were centrifuged at  $20,000 \times g$  for 15 min at  $4^\circ\text{C}$  and the supernatant was collected into a 100 mL volumetric flask. One mL of the extract was filtered through a membrane filter ( $0.45 \mu\text{m}$ , Macherey Nagel, Germany) and a  $20 \mu\text{L}$  sample was used for HPLC analysis of ascorbic acid. Extracts were analyzed using a liquid chromatograph equipped with a diode array detector monitoring at  $254 \text{ nm}$ . Separations were achieved on an Luna C18 (2) column ( $4.6 \text{ mm} \times 150 \text{ mm}$ ,  $5 \mu\text{m}$ ) fitted with a guard column ( $4 \text{ mm} \times 3.0 \text{ mm}$ ,  $5 \mu\text{m}$ ) of the same material (Phenomenex, CA). HPLC elution was carried out at  $30^\circ\text{C}$  using  $20 \text{ mM KH}_2\text{PO}_4$  pH 3.0/Acetonitrile (95:5) as the mobile phase at a flow rate of  $0.7 \text{ mL min}^{-1}$ . Results were expressed as  $\text{mg ascorbic acid } 100 \text{ g}^{-1}$  of fresh weight.

For organic acids and sugars, fruit were stoned and homogenized with a manual blender. Twenty grams of mashed fruit were weighed and homogenized at medium speed for 5 min with 80 mL of deionized water and then shaken for 30 min. The homogenates were centrifuged at  $20,000 \times g$  for 20 min at  $30^\circ\text{C}$  and the supernatant was collected into a 100 mL volumetric flask. One mL of the extract was filtered through a membrane filter ( $0.45 \mu\text{m}$ , Macherey Nagel, Germany) and a  $20 \mu\text{L}$  sample was used for HPLC analysis of sugars (glucose, fructose) and organic acids (malic, succinic, quinic, oxalic and citric).

Organic acids were analyzed isocratically with Rezex ROA-Organic Acid H+ (8%) ( $8 \mu\text{m}$ ,  $300 \text{ mm} \times 7.8 \text{ mm}$  I.D. Phenomenex) column. HPLC elution was carried out at  $55^\circ\text{C}$  using  $0.005 \text{ N Sulfuric acid}$  as the mobile phase at a flow rate of  $0.5 \text{ mL min}^{-1}$ . Organic acids were identified and quantified by using a UV detector with wavelength set at  $210 \text{ nm}$  and by comparison of retention times and peak areas with standard solutions of known organic acids. The contents were expressed as  $\text{mg } 100 \text{ g}^{-1}$  of fresh weight.

Sugars were analyzed isocratically with a Rezex RCM column ( $5 \mu\text{m}$ ,  $300 \text{ mm} \times 7.8 \text{ mm}$ , Phenomenex) at  $80^\circ\text{C}$  using an RI detector. Deionized water was used as the mobile phase, with an injection volume of  $20 \mu\text{L}$ , and a flow rate of  $0.6 \text{ mL min}^{-1}$ . The contents were expressed as  $\text{mg } 100 \text{ g}^{-1}$  of fresh weight.

Authentic standard compounds were purchased from Merck KGaA (Darmstadt, Germany) and Sigma-Aldrich (Chimie S.a.r.l., Lyon, France). For ascorbic acid, organic acids and sugars quantification, external standard calibration curves for the identified components. Five injections were made for each calibration level. For the linear regression of the curves of external calibration standards,  $r^2$  values were between 0.995 and 0.999.

## 2.12. Statistical analysis

The research was conducted using a randomized factorial experimental design. The factors were 1-MCP concentration and storage time (0, 15, 30, 45, 60 days). The data were analyzed using the Statistical Analysis System software program, version 9.0 (SAS Inst., Cary, NC, USA) and treatments means were statistically compared using Duncan's multiple range test ( $P \leq 0.05$ ). When the interactions were found not significant, overall value (means) and their comparisons were used.

## 3. Results and discussion

### 3.1. Weight loss

The weight loss in control and 1-MCP treated medlars increased during the whole storage period (Table 1). Fruit treated with 1-MCP at any concentrations examined had lower weight losses than controls. At 60 days of storage, weight loss of the control medlars reached the maximum of 1.82%, whereas that of  $0.6 \mu\text{L L}^{-1}$  1-MCP treated medlars reached values of 1.32%. This result suggests that

$0.6 \mu\text{L L}^{-1}$  1-MCP treatment in palliflex storage system was quite effective at reducing weight loss. Similar effects of 1-MCP or/and CA storage on reducing of weight loss of fruit have been observed for pear (Mahajan et al., 2010), litchi (Sivakumar and Korsten, 2010) and high bush blueberry (Chiabrando and Giacalone, 2011).

### 3.2. Taste

After 30, 45 and 60 days of storage, fruit were tested using taste panels. After 30 days of storage, there were no significant differences between control and 1-MCP treatments on taste scores. However, after 45 and 60 days of storage, the medlars treated with 0.4 and  $0.6 \mu\text{L L}^{-1}$  1-MCP had higher taste scores than  $0.2 \mu\text{L L}^{-1}$  1-MCP treated and control fruit (Table 1). In all treatments, fruit were still of acceptable taste at the end of the storage. The taste of the fruit depend upon the complex interaction of sugars, organic acids, phenolics and more specialized flavor compounds (Tucker, 1993). Of these components, sugars are one of the most important affecting fruit taste and quality, since composition and amount of accumulated sugars in fruit directly influences sweetness (Itai and Tanahashi, 2008).

### 3.3. Flesh firmness

Flesh firmness of medlar fruit is one of the most common physiological parameters to assess the progress of fruit softening and ripening. It directly affects postharvest life and commercial market value of the medlars. During storage, firmness values of all the treatments decreased with storage time. These decreases were more pronounced in control and  $0.2 \mu\text{L L}^{-1}$  1-MCP treated fruit than 0.4 and  $0.6 \mu\text{L L}^{-1}$  1-MCP treated fruit. The maximum retention in firmness was obtained from the fruit treated with 0.4 and  $0.6 \mu\text{L L}^{-1}$  1-MCP, with 8.61 N and 8.93 N firmness values (overall), respectively (Table 1). These data clearly indicated that 0.4 and  $0.6 \mu\text{L L}^{-1}$  1-MCP treatments after harvest delayed medlar fruit softening at  $0^\circ\text{C}$ . Retention of firmness is very important for long term storage of medlars, because this fruit is very susceptible to softening, in contrast to many other horticultural crops. Tissue softening of fruit and vegetables is the most apparent change that occurs after harvest. Generally, the loss of fruit firmness during storage occurs mainly due to the change of water-insoluble protopectins into water-soluble pectins (Kays, 1991). Medlar fruit is characterized by rapid softening after harvest, which is the major factor limiting postharvest life of medlars (Selcuk and Erkan, 2015). The present work showed that 1-MCP treatments inhibited the decline in fruit firmness. This can be attributed to the function of ethylene in regulating the activity of softening-related metabolism (Jeong et al., 2003) and this suggests a decrease in activity of softening enzymes induced by 1-MCP (Lohani et al., 2004). Similar effects of 1-MCP on delaying the softening of fruit have been observed for guava (Singh and Pal, 2008), apple (Fawbush et al., 2009), cherimoya (Li et al., 2009), pear (Mahajan et al., 2010; Li et al., 2013), mangosteen (Piriyavinit et al., 2011), goldenberry (Valdenegro et al., 2012), plum (Singh and Singh, 2012; Minas et al., 2013), avocado (Zhang et al., 2011), litchi (Sivakumar and Korsten, 2010), high bush blueberry (Chiabrando and Giacalone, 2011) and jujube (Zhang et al., 2012).

### 3.4. Decay incidence and external browning index

No signs of decay were observed in palliflex storage system during entire storage period. However, external browning is also an important problem during storage of medlar fruit. The external browning of control and 1-MCP treated fruit appeared at 30 days after storage and then progressively increased as storage duration increased (Table 1). The 0.4 and  $0.6 \mu\text{L L}^{-1}$  1-MCP treated fruit showed slight browning incidence at 30 days after storage

**Table 1**Weight loss, taste, firmness, external browning index,  $L^*$ ,  $C^*$  and  $h^o$  values, pH, total titratable acidity and total soluble solids of 'Istanbul' medlars during cold storage.

Testing index	Treatments	Storage time (days)					
		Day 0	Day 15	Day 30	Day 45	Day 60	Overall
Weight loss (%)	Control	-	0.41k	0.89h	1.38d	1.82a <sup>a</sup>	1.12A <sup>b</sup>
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	-	0.20l	0.65i	1.18f	1.68b	0.93B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	-	0.18l	0.61i	1.06g	1.44c	0.82C
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	-	0.12m	0.49j	0.90h	1.32e	0.71D
	Overall		0.22d	0.66c	1.13b	1.57a	
Taste <sup>c</sup>	Control	-	-	4.20bc	3.60cd	2.60e	3.47B
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	-	-	4.20bc	4.40ab	3.00de	3.87B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	-	-	4.00bc	5.00a	4.40ab	4.47A
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	-	-	4.00bc	5.00a	4.40ab	4.47A
	Overall			4.10b	4.50a	3.60c	
Firmness (Newton)	Control	14.77a	11.65b	4.99de	3.20ef	0.71g	7.06C
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	14.77a	12.48b	6.81cd	4.67e	1.37fg	8.02B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	14.77a	12.67b	7.30c	6.82cd	1.50fg	8.61AB
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	14.77a	12.75b	7.70c	7.45c	1.99fg	8.93A
	Overall	14.77a	12.39b	6.70c	5.53d	1.39e	
Browning index <sup>d</sup>	Control	1.00g	1.00g	3.00cd	4.67a	5.00a	2.93A
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	1.00g	1.00g	2.67de	4.00b	5.00a	2.73B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	1.00g	1.00g	2.33ef	3.33c	5.00a	2.53C
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	1.00g	1.00g	2.00f	3.00cd	5.00a	2.40C
	Overall	1.00d	1.00d	2.50c	3.75b	5.00a	
$L^*$	Control	56.60a	54.27b	53.94b	47.50cd	44.45e	51.35A
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	56.60a	54.31b	54.22b	48.40c	45.16e	51.74A
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	56.60a	54.33b	54.26b	48.62c	45.48de	51.86A
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	56.60a	54.75ab	54.54ab	49.05c	46.12de	52.21A
	Overall	56.60a	54.41b	54.24b	48.39c	45.30d	
$C^*$	Control	38.56a	35.53a	29.56c	21.67de	18.49f	28.76B
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	38.56a	37.45a	29.69c	21.82de	18.81f	29.27B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	38.56a	37.25a	32.65b	22.05de	19.28ef	29.96AB
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	38.56a	37.39a	32.83b	24.26d	20.33ef	30.67A
	Overall	38.56a	36.90b	31.19c	22.45d	19.23e	
$h^o$	Control	83.54a	82.50a	79.45a	66.47c	57.54d	73.90B
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	83.54a	82.97a	80.34a	66.55c	57.84d	74.25B
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	83.54a	83.17a	81.66a	71.27b	61.30d	76.19A
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	83.54a	83.48a	82.27a	72.40b	65.57c	77.45A
	Overall	83.54a	83.03a	80.93b	69.17c	60.56d	
TA (% malic acid)	Control	1.18a	1.15a	0.90b	0.75cd	0.61e	0.92B
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	1.18a	1.16a	1.10a	0.82bc	0.62e	0.98A
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	1.18a	1.15a	1.12a	0.85b	0.67de	1.00A
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	1.18a	1.17a	1.14a	0.87b	0.70de	1.01A
	Overall	1.18a	1.16a	1.06b	0.82c	0.65d	
TSS (%)	Control	15.17f	16.00cde	16.73abc	17.00ab	16.67abc	16.23A
	0.2 $\mu\text{L L}^{-1}$ 1-MCP	15.17f	16.00cde	16.67abc	16.83ab	17.17a	16.37A
	0.4 $\mu\text{L L}^{-1}$ 1-MCP	15.17f	15.83def	16.50ad	16.67abc	17.17a	16.27A
	0.6 $\mu\text{L L}^{-1}$ 1-MCP	15.17f	15.67ef	16.33be	16.67abc	16.83ab	16.13A
	Overall	15.17d	15.88c	16.56b	16.79ab	16.96a	

TA, total titratable acidity; TSS, total soluble solids.

<sup>a</sup> Means in the same row with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.<sup>b</sup> Means in the same column with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.<sup>c</sup> The taste analysis was conducted on the base of a 5 point hedonic scale, where: 1 = very poor; 2 = poor (limit of acceptability); 3 = good; 4 = very good; 5 = excellent.<sup>d</sup> The external browning index (EBI) was rated as 1 = none (excellent quality); 2 = slight (browning area <5%); 3 = moderate (browning area 5–25%); 4 = moderately severe (browning area 25–50%); 5 = extreme (browning area >50%).

and their browning indices were lower than those of both control and 0.2  $\mu\text{L L}^{-1}$  1-MCP treated fruit. The treatments with 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP had the strongest inhibitory effect on external browning (overall values), although after 60 days of storage all fruit in all treatments had skin external browning. Polyphenol oxidase (PPO) and phenolics are responsible for some of the enzymatic browning in fruit and vegetables (Mayer and Harel, 1979). The high degree of susceptibility to browning of medlar fruit are mostly due to its high concentration of phenolics. Browning symptoms in medlars result from the oxidation of polyphenols by PPO (Aydin and Kadioglu, 2001; Dincer et al., 2002; Ayaz et al., 2008). In this study, the increases external skin browning was correlated with a reduction in total phenolics. Similar results were also obtained by Selcuk

and Erkan (2015). It has been reported that levels of PPO and phenolics may change during fruit development and ripening which may influence the potential damage in loquat fruit (Cai et al., 2006).

### 3.5. Color

The most important factor during marketing of fruit and vegetables for consumers is color. During storage, skin color changes of control and 1-MCP treated groups are shown in Table 1. At the beginning of storage, all the fruit had values of 56.60 for  $L^*$ , 38.56 for  $C^*$  and 83.54 for  $h^o$  (Table 1). In this study, storage time affected the color and  $L^*$ ,  $C^*$  and  $h^o$  values linearly decreased during the storage period. The decline in  $C^*$  and  $h^o$  values was slower at 0.4 and

**Table 2**

Total phenolic, total flavonoid, total condensed tannin, and ascorbic acid concentrations and antioxidant activity of 'Istanbul' medlars during cold storage.

Testing index	Treatments	Storage time (days)					
		Day 0	Day 15	Day 30	Day 45	Day 60	Overall
Total phenolic contents (mg GAE 100 g <sup>-1</sup> fw)	Control	985.03a	776.30bcd	658.85d	301.15ef	83.73g <sup>a</sup>	561.01B <sup>b</sup>
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	985.03a	822.48bc	698.18cd	347.51e	98.64g	590.37B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	985.03a	900.91ab	716.36cd	357.55e	114.27g	614.82AB
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	985.03a	965.64a	737.88cd	432.00e	193.55fg	662.82A
	Overall	985.03a	866.33b	702.82c	359.55d	122.55e	
Total flavonoid contents (mg CE 100 g <sup>-1</sup> fw)	Control	1085.65a	724.07c	659.48c	263.68d	43.97e	555.37C
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	1085.65a	868.44b	677.81c	280.10d	77.30e	597.86BC
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	1085.65a	1015.37a	695.11c	300.54d	79.86e	635.30AB
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	1085.65a	1030.13a	708.00c	358.02d	92.16e	654.79A
	Overall	1085.65a	909.50b	685.10c	300.58d	73.32e	
Total condensed tannin contents (mg CE 100 g <sup>-1</sup> fw)	Control	1385.87a	915.82cd	899.98d	248.86ef	62.99g	702.70C
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	1385.87a	1192.54b	904.32d	273.72ef	86.57g	768.61B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	1385.87a	1301.08a	1027.06cd	294.49e	92.95g	820.29AB
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	1385.87a	1340.11a	1053.04c	333.97e	142.62fg	851.12A
	Overall	1385.87a	1187.39b	971.10c	287.76d	96.28e	
Ascorbic acid contents (mg 100 g <sup>-1</sup> fw)	Control	12.10a	7.53c	3.17d	1.14efg	0.75g	4.94B
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	12.10a	8.33bc	3.90d	1.53efg	0.75g	5.32AB
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	12.10a	8.98b	4.15d	1.97ef	0.77g	5.59A
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	12.10a	9.19b	4.32d	2.04e	0.86fg	5.70A
	Overall	12.10a	8.51b	3.88c	1.67d	0.78e	
EC <sub>50</sub> values <sup>c</sup> (mg fw mg <sup>-1</sup> DPPH)	Control	4.33e	6.91e	7.59e	20.09d	43.35a	16.45A
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	4.33e	4.69e	7.47e	18.62d	39.08b	14.84B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	4.33e	4.72e	7.11e	17.67d	36.23b	14.01B
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	4.33e	4.52e	6.92e	17.40d	27.38c	12.11C
	Overall	4.33d	5.21d	7.27c	18.45b	36.51a	

<sup>a</sup> Means in the same row with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.<sup>b</sup> Means in the same column with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.<sup>c</sup> EC<sub>50</sub> of Trolox was determined as  $0.12 \pm 0.01$  mg mg<sup>-1</sup> DPPH.

0.6  $\mu\text{LL}^{-1}$  1-MCP treated fruit than control and 0.2  $\mu\text{LL}^{-1}$  1-MCP treated fruit (overall values). When harvested the color of fruit is still greenish brown, however, on day 30, the color had changed to brownish, by day 45 the color was dark brown and by day 60 it was blackish brown color. These changes occurred much slower in 0.4 and 0.6  $\mu\text{LL}^{-1}$  1-MCP treated fruit than control and 0.2  $\mu\text{LL}^{-1}$  1-MCP treated fruit. Also, 1-MCP delayed color changes in mangosteen (Piriayavinit et al., 2011), pear (Li et al., 2013) and plum (Minas et al., 2013).

### 3.6. Titratable acidity, and total soluble solids

Malic acid is the major organic acid in medlar fruit (Selcuk and Erkan, 2015). The titratable acidity (TA) decreased during the storage period in both the 1-MCP treated and control fruit. However, these decreases were much slower in 1-MCP treated fruit (overall values) (Table 1). TA is directly related to the amount of organic acids present in the fruit, and a reduction in acidity may be expected as a result of metabolic changes in fruit or due to the use of organic acids in the respiratory process (Maftoonazad et al., 2008). TA loss was significantly delayed or maintained by 1-MCP in guava (Singh and Pal, 2008), jujube (Zhang et al., 2012), pear (Li et al., 2013) and plum, (Minas et al., 2013).

Total soluble solids (TSS) is a critical factor for determining fruit quality and consumer acceptability in horticultural products. TSS content of 1-MCP treated and control fruit during storage are shown in Table 1. TSS levels at the beginning of storage were 15.17% and increased gradually during storage in control and 1-MCP treated medlars. As in our study, in other fruit such as persimmon (Salvador et al., 2004), guava (Bassetto et al., 2005), goldenberry (Gutierrez et al., 2008) and plum (Minas et al., 2013), soluble solids were not affected by 1-MCP treatments. Delay in the increase of TSS content was reported for high bush blueberry (Chiabrando and Giacalone, 2011), jujube (Zhang et al., 2012), guava (Singh and Pal, 2008), pear (Li et al., 2013), and broccoli (Fernández-León et al., 2013).

### 3.7. Total phenolic contents, total flavonoid contents, total condensed tannins, ascorbic acid and antioxidant activity

The contents of total phenolics and total flavonoids decreased during the storage period in all 1-MCP treated medlars as well as control fruit (Table 2). In general, 0.4 and 0.6  $\mu\text{LL}^{-1}$  1-MCP treatments delayed the contents of total phenolics and total flavonoids decrease. The 0.4 and 0.6  $\mu\text{LL}^{-1}$  1-MCP were the most effective treatments in maintaining higher levels of total phenolics and total flavonoids (overall values) during storage period. The reduction in loss of phenolics by 1-MCP treatments are consistent with the retard of fruit ripening and senescence. It has been reported that 1-MCP prevents or delays loss of total phenolics in goldenberry (Valdenegro et al., 2012), plum (Singh and Singh, 2012), pear (Li et al., 2013) and broccoli (Fernández-León et al., 2013). Total phenolics and total flavonoids contents declined and external browning increased over the 60 days of storage period. A significant negative correlation was observed between total phenolics contents and the external browning index (data not shown). Ayaz et al. (2008) mentioned that as the medlars ripening progressed through ripe to over-ripe, there was an apparent gradual decrease in the total phenolic concentrations, which is connected with an increased PPO activity.

Medlar fruit contain a large amount of condensed tannins which has an astringent taste (Selcuk and Erkan, 2015). In flavor, phenolic compounds are major substances responsible of astringency, in which tannins, catechins, and epicatechins have been identified as astringent molecules (Clifford et al., 1997). In the present work, a high level of total condensed tannins was determined in medlar fruit (1385.87 mg CE 100 g<sup>-1</sup> fw) at harvest. The total condensed tannins declined gradually in both control and 1-MCP treated fruit during storage. The reduction in this important metabolite could be slowed by using different storage techniques. The decrease in total condensed tannins was lower in 1-MCP treated medlars than in control fruit (Table 2). But it is clear that applications of 0.4

**Table 3**

Organic acid and sugar contents of 'Istanbul' medlars during cold storage.

Testing index	Treatments	Storage time (days)					
		Day 0	Day 15	Day 30	Day 45	Day 60	Overall
Malic acid (mg 100 g <sup>-1</sup> fw)	Control	1919a	1841ab	1645d	1239g	1192g <sup>a</sup>	1567C <sup>b</sup>
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	1919a	1856ab	1678cd	1344ef	1276fg	1615B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	1919a	1877a	1736cd	1363ef	1286fg	1636AB
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	1919a	1880a	1772bc	1390e	1340ef	1660A
	Overall	1919a	1864b	1708c	1334d	1273e	
Succinic acid (mg 100 g <sup>-1</sup> fw)	Control	596.93a	531.32abc	511.37be	476.68cde	442.81e	511.8A
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	596.93a	523.25ad	516.77be	478.17cde	445.09de	512.0A
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	596.93a	535.14abc	520.07ae	483.64be	448.38de	516.8A
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	596.93a	561.02ab	549.06abc	498.60be	475.45cde	536.2A
	Overall	596.9a	537.7b	524.3b	484.3c	452.9c	
Quinic acid (mg 100 g <sup>-1</sup> fw)	Control	789.86a	773.67a	723.67a	716.30a	559.53b	712.60A
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	789.86a	756.74a	731.16a	719.04a	563.74b	712.11A
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	789.86a	765.10a	742.02a	723.06a	580.08b	720.02A
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	789.86a	776.65a	758.70a	737.60a	591.46b	730.85A
	Overall	789.86a	768.04ab	738.89ab	724.00b	573.70c	
Oxalic acid (mg 100 g <sup>-1</sup> fw)	Control	45.62a	42.79a	31.78b	27.25bcd	22.87d	34.06B
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	45.62a	43.21a	32.36b	28.92bcd	23.91cd	34.80B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	45.62a	44.36a	33.19b	29.94bcd	26.78bcd	35.98AB
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	45.62a	44.68a	43.16a	30.50bc	27.59bcd	38.31A
	Overall	45.62a	43.76a	35.12b	29.15c	25.29d	
Citric acid (mg 100 g <sup>-1</sup> fw)	Control	22.96a	14.14d	9.35f	4.13h	3.07h	10.73C
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	22.96a	16.50bc	11.60e	6.06g	3.41h	12.10B
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	22.96a	16.66bc	11.93e	6.17g	3.78h	12.30B
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	22.96a	17.08b	15.51c	6.24g	4.15h	13.19A
	Overall	22.96a	16.09b	12.10c	5.65d	3.60e	
Fructose (mg 100 g <sup>-1</sup> fw)	Control	7654a	7988a	8011a	8033a	7657a	7869A
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	7654a	7984a	8093a	8108a	7951a	7958A
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	7654a	7891a	7897a	7908a	8074a	7885A
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	7654a	7890a	8004a	8082a	8108a	7948A
	Overall	7654b	7938a	8001a	8033a	7948a	
Glucose (mg 100 g <sup>-1</sup> fw)	Control	6095e	6987a	6551bcd	6301cde	6048e	6396A
	0.2 $\mu\text{LL}^{-1}$ 1-MCP	6095e	6888ab	6839ab	6609abc	6070e	6500A
	0.4 $\mu\text{LL}^{-1}$ 1-MCP	6095e	6817ab	6785ab	6566bcd	6220de	6496A
	0.6 $\mu\text{LL}^{-1}$ 1-MCP	6095e	6871ab	6731ab	6595ad	6279cde	6514A
	Overall	6095c	6891a	6727a	6518b	6154c	

<sup>a</sup> Means in the same row with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.<sup>b</sup> Means in the same column with different letters are significantly different at  $P \leq 0.05$  by Duncan's multiple range test.

and 0.6  $\mu\text{LL}^{-1}$  1-MCP resulted in better preservation of condensed tannins in medlars during postharvest storage (overall values). Tannins are polyphenolic secondary metabolites of higher plants. Tannins are usually divided into the flavonoid derived condensed tannins, and into hydrolysable tannins (Khanbabaee and Ree, 2001). Condensed and hydrolysable tannins of relatively high molecular weight have also been shown to be effective antioxidants with greater activity than simple phenolics (Hagerman et al., 1998). The quantity and quality of polyphenols present in plant foods can vary greatly due to factors such as plant genetics, soil composition and growing conditions, state of maturity and postharvest conditions (Faller and Fialho, 2009).

Though an overall decrease in ascorbic acid content was observed during storage, it was retained at higher levels in 1-MCP-treated fruit. After 60 days of storage, the control fruit showed lower amounts of ascorbic acid, while the concentrations of 0.4 or 0.6  $\mu\text{LL}^{-1}$  1-MCP caused a delay in this decrease the ascorbic acid content. 1-MCP treatments had resulted higher amount of ascorbic acid contents at the end of storage period (overall values). The preservation of higher ascorbic acid contents might have resulted from the 1-MCP-induced retarded ripening in medlar fruit (Tables 1 and 2). Similar observations were reported in guava (Singh and Pal, 2008), goldenberry (Valdenegro et al., 2012), jujube (Zhang et al., 2012), pear (Li et al., 2013) and broccoli (Fernández-León

et al., 2013). However, ascorbic acid contents were unaffected by 1-MCP treatments in guava (Bassetto et al., 2005) and goldenberry (Gutierrez et al., 2008).

The EC<sub>50</sub> parameter was widely used by different authors to measure the antioxidant power (Vinson et al., 1995; Brand-Williams et al., 1995), and according to them, the lower EC<sub>50</sub> reflects the higher antioxidant power. The initial EC<sub>50</sub> value at harvest was 4.33 mg fw mg<sup>-1</sup> DPPH and increased in control fruit to 7.59 mg fw mg<sup>-1</sup> DPPH, within 30 days, reaching around 43.35 mg fw mg<sup>-1</sup> DPPH at 60 days (Table 2). After 60 days of storage, EC<sub>50</sub> values of fruit treated with 0.6  $\mu\text{LL}^{-1}$  1-MCP reached 27.38 mg fw mg<sup>-1</sup> DPPH (the highest antioxidant activity). In the present study, we have found that the over-ripe fruit also lost its functional properties and antioxidant capacity. However, the decrease was smaller in 0.6  $\mu\text{LL}^{-1}$  1-MCP treated fruit than in the other treatments and control fruit at the end of storage in palliflex system (60 days). Our results suggest that 0.6  $\mu\text{LL}^{-1}$  1-MCP treatment enables medlars to maintain a high level of antioxidant activity. Previous studies on the effect of 1-MCP on the antioxidant activity of fruit during storage in different conditions are contradictory. Chiabrando and Giacalone (2011) showed that 1-MCP treatment had no effect on the antioxidant activity in high bush blueberry, while Sun et al. (2012) and Hoang et al. (2011) found higher antioxidant activity in 1-MCP treated Chinese kale



and apple. The inconsistency in antioxidant activity results during storage may be caused by the different cultivars, storage conditions and the analytical methods used (Hoang et al., 2011).

There is increasing evidence that consumption of a variety of phenolic compounds present in natural foods may lower the risk of serious health disorders because of the antioxidant activity of these compounds (Hertog et al., 1993). Medlars are rich sources of dietary phenolics with antioxidant properties that are associated with a wide range of health benefits (Gruz et al., 2011; Nabavi et al., 2011; Gulcin et al., 2011). Our study indicates that total phenolics, total flavonoids, total condensed tannins and ascorbic acid are an important antioxidants in medlar fruit, and those are critical factors in determining the quality of medlars.

### 3.8. Organic acids and sugars content

The changes in organic acids content of medlars during storage at 0 °C are shown in Table 3. Four major organic acids, consisting of malic, succinic, quinic, oxalic and citric acid were detected in the 'Istanbul' medlars during storage. This study indicates that malic acid is the most abundant organic acid, followed by succinic, quinic, oxalic and citric acids in medlars, as reported previously in other medlar cultivars (Romero-Rodriguez et al., 2000; Glew et al., 2003a,b; Selcuk and Erkan, 2015).

In general, a gradual decrease in malic acid content was observed during the entire storage period (Table 3). However, in control fruit the contents of malic acid were lower as compared to 1-MCP treated fruit, and the rate of reduction in malic acid content was directly proportional to the concentrations of the 1-MCP treatments, whereas the highest contents of malic acid were observed in 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit (overall values). The present results revealed that 1-MCP treatments influenced the internal quality of medlars resulting in the delay of fruit softening and organic acids degradation. Similar changes in malic acid contents during storage were reported in apple (Defilippi et al., 2004; Bai et al., 2005). Because organic acids are substrates of respiration, their levels typically decrease as a result of ripening related metabolism during the postharvest period (Bai et al., 2005). It is also believed that 1-MCP treatments reduce the rate of respiration and may therefore delay the utilization of organic acids (Defilippi et al., 2004).

Succinic and quinic acids contents decreased in all treatments during whole storage period (Table 3).

The oxalic and citric acid contents of fruit declined during storage (Table 3). The highest oxalic acid content were in 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit, whereas, it was the lowest in control and 0.2  $\mu\text{L L}^{-1}$  1-MCP treated fruit on day 60 (overall values). The highest citric acid content was in 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit, whereas, it was lowest in control fruit on day 60 (overall values). The fruit treated with 1-MCP maintained higher citric acid during storage probably due to delay in ripening process. Higher levels of organic acids are expected in less ripe fruit, and a decrease is expected through ripening and senescence (Mao et al., 2007). 1-MCP is known to delay ripening (Blankenship and Dole, 2003). Antunes et al. (2010) observed lower citric acid loss during storage in kiwifruit treated with 1-MCP. Similar changes in citric acids contents during storage were reported in apple (Defilippi et al., 2004).

Fructose, glucose and sucrose were the main soluble components in medlar mesocarp tissue, as previously reported (Romero-Rodriguez et al., 2000; Aydin and Kadioglu, 2001; Glew et al., 2003a,b). The composition of these three sugars plays a key role in determining the sweetness of medlar fruit. In the present study, fructose was the major sugar present in medlar fruit followed by glucose and sucrose. Sucrose was detected, but was at or below the limit of quantification in almost all samples and thus they were

not considered. During storage, sucrose content declined rapidly (data not shown). It is probable that sucrose was hydrolyzed during storage, yielding glucose and fructose. Glew et al. (2003b) reported high levels of sucrose at 1 week after harvest and decreased at 2 and 3 weeks after harvest.

In control and 0.2  $\mu\text{L L}^{-1}$  1-MCP treated fruit, fructose content increased during the 45 days of storage then decreased for the rest of the storage period. Apparently, this increase is a result of the ripening process. On the other hand, the fructose content of 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit increased during the whole storage period. After 60 days of storage, the medlars treated with 0.6  $\mu\text{L L}^{-1}$  1-MCP had higher fructose content than the other 1-MCP treated and control fruit probably due to delayed fruit ripening at 0.6  $\mu\text{L L}^{-1}$  1-MCP (Table 3). However, there were no significant differences between control and 1-MCP treatments on fructose content. Glew et al. (2003b) found higher levels of fructose and glucose at 2 weeks after harvest than at 1 week after harvest in 'Dutch' medlars.

The glucose content increased until the 15 days of storage then decreased in all treatments (Table 3). The highest glucose contents were recorded in the 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit after 60 days of storage. Similar to fructose content, there were no significant differences between control and 1-MCP treatments on fructose content. The decreases in sugars content during ripening and during storage of medlars have already been reported by others (Glew et al., 2003a,b; Selcuk and Erkan, 2015).

In conclusion, this study is the first report on antioxidant activity, organic acids and sugars changes in medlar fruit in response to 1-MCP. There were profound changes in texture, color, flavor and antioxidant activity during medlar storage life, leading to over-ripening. However, our results show that 1-MCP is effective at delaying ripening of medlar fruit at low temperature, and subsequent ripening was not impaired during long term storage. 1-MCP treatment at 0.4 and 0.6  $\mu\text{L L}^{-1}$  at 0 °C temperature maintained the postharvest life, delayed weight loss and loss of taste, slowed softening and skin browning, as well as reduced the changes in  $C^*$  and  $h^0$  values of the medlars. 1-MCP treatments also retarded the decline of titratable acidity. Furthermore, 0.4 and 0.6  $\mu\text{L L}^{-1}$  1-MCP treatment reduced the decreases of total phenolics, total flavonoids, total condensed tannins, ascorbic acid, as well as individual organic acids (malic and oxalic acids) in medlars. Moreover, 0.6  $\mu\text{L L}^{-1}$  1-MCP treated fruit maintained higher antioxidant activity and citric acid contents. To the best of our knowledge, this is the first study reporting the successful application of 1-MCP treatment on medlar fruit. Our results suggest that 1-MCP treatment in palliflex storage system may be a promising technique to extend postharvest life and maintain quality of medlars.

### Acknowledgments

The authors wish to acknowledge the financial support given by the Scientific and Technological Research Council of Turkey (Project no: TOVAG 111O504). The authors gratefully acknowledge the support from AgroFresh Inc. (Rohm and Haas Inc., Turkey) for supplying SmartFresh™ product. The authors thank Dr. Susan Lurie for critical review of the manuscript.

### References

- Antunes, M.D.C., Dandlen, S., Cavaco, A.M., Miguel, G., 2010. Effects of postharvest application of 1-MCP and postcutting dip treatment on the quality and nutritional properties of fresh-cut kiwifruit. *J. Agric. Food Chem.* 58, 6173–6181.
- Ayaz, F.A., Glew, R.H., Huang, H.S., Chuang, L.T., Vanderjagt, D.J., Strnad, M., 2002. Evolution of fatty acids in medlar (*Mespilus germanica* L.) mesocarp at different stages of ripening. *Grasas Aceites* 352, 352–356.
- Ayaz, F.A., Demir, O., Torun, H., Kolcuoglu, Y., Colak, A., 2008. Characterization of polyphenoloxidase (PPO) and total phenolic contents in medlar (*Mespilus germanica* L.) fruit during ripening and over ripening. *Food Chem.* 106, 291–298.



- Aydin, N., Kadioglu, A., 2001. Changes in the chemical composition, polyphenol oxidase and peroxidase activities during development and ripening of medlar fruits (*Mespilus germanica* L.). *Bulg. J. Plant Physiol.* 27, 85–92.
- Bai, J.H., Baldwin, E.A., Goodner, K.L., Mattheis, J.P., Brecht, J.K., 2005. Response of four apple cultivars to 1-methylcyclopropene treatment and controlled atmosphere storage. *HortScience* 40, 1534–1538.
- Bassetto, E., Jacomino, A.P., Pinheiro, A.L., Kluge, R.A., 2005. Delay of ripening of 'Pedro Sato' guava with 1-methylcyclopropene. *Postharvest Biol. Technol.* 35, 303–308.
- Baytop, T., 1999. Türkiye'de bitkiler ile tedavi, geçmişte ve bugün (Therapy with Medicinal Plants in Turkey, Past and Present), 2nd ed. Nobel Tip Kitabevi, Istanbul, pp. 299.
- Blankenship, S.M., Dole, J.M., 2003. 1-Methylcyclopropene: a review. *Postharvest Biol. Technol.* 28, 1–25.
- Brand-Williams, W., Cuvelier, M.E., Berset, C., 1995. Use of a free radical method to evaluate antioxidant activity. *Food Sci. Technol.* 28, 25–30.
- Broadhurst, R.B., Jones, W.T., 1978. Analysis of condensed tannins using acidified vanillin. *J. Sci. Food Agric.* 29, 788–794.
- Browicz, K., 1972. *Mespilus* L. In: Davis, P.H. (Ed.), *Flora of Turkey and the East Aegean Islands*, vol. 4. Edinburgh University Press, Edinburgh, pp. 128–129.
- Cai, C., Chen, K., Xu, W., Zhang, W., Li, X., Ferguson, I., 2006. Effect of 1-MCP on postharvest quality of loquat fruit. *Postharvest Biol. Technol.* 40, 155–162.
- Chang, C.H., Lin, H.Y., Chang, C.Y., Liu, Y.C., 2006. Comparisons on the antioxidant properties of fresh, freeze-dried and hot-air-dried tomatoes. *J. Food Eng.* 77, 478–485.
- Chiabrando, V., Giacalone, G., 2011. Shelf-life extension of highbush blueberry using 1-methylcyclopropene stored under air and controlled atmosphere. *Food Chem.* 126, 1812–1816.
- Clifford, M.N., 1997. Astringency. In: Tomas-Barberán, F.A., Robins, R.J. (Eds.), *Phytochemistry of Fruit and Vegetables*. Oxford University Press, New York, pp. 87–107.
- Defilippi, B.G., Dandekar, A.M., Kader, A.A., 2004. Impact of suppression of ethylene action or biosynthesis on flavor metabolites in apple (*Malus domestica* Borkh) fruits. *J. Agric. Food Chem.* 52, 5694–5701.
- Dincer, B., Colak, A., Aydin, N., Kadioglu, A., Guner, S., 2002. Characterization of polyphenol oxidase from medlar fruits (*Mespilus germanica* L. Rosaceae). *Food Chem.* 77, 1–7.
- Dirr, M.A., 1990. *Manual of Woody Landscape Plants: Their Identification, Ornamental Characteristics, Culture, Propagation and Uses*, 4th ed. Stipes Publishing Co., Champaign, IL, pp. 554.
- Dogan, A., Erkan, M., 2014. Bahçe Ürünlerinin Muhafazasında Yeni Bir Teknoloji: Palistore (Palliflex) Ortamında Depolama (A new storage technology: palistore (palliflex) storage system for horticultural crops). *Meyve Bilim.* 1, 1–6.
- Faller, A.L.K., Fialho, E., 2009. The antioxidant capacity and polyphenol content of organic and conventional retail vegetables after domestic coking. *Food Res. Int.* 42, 210–215.
- Fawbush, F., Nock, J.F., Watkins, C.B., 2009. Antioxidant contents and activity of 1-methylcyclopropene (1-MCP)-treated 'Empire' apples in air and controlled atmosphere storage. *Postharvest Biol. Technol.* 52, 30–37.
- Fernández-León, M.F., Fernández-León, A.M., Lozano, M., Ayuso, M.C., González-Gómez, D., 2013. Different postharvest strategies to preserve broccoli quality during storage and shelf life: controlled atmosphere and 1-MCP. *Food Chem.* 138, 564–573.
- Gadow, A.V., Joubert, E., Hansmann, C.F., 1997. Comparison of the antioxidant activity of rooibos tea (*Aspalathus linearis*) with green oolong and black tea. *Food Chem.* 60, 73–77.
- Glew, R.H., Ayaz, F.A., Sanz, C., Vanderjagt, D.J., Huang, H.S., Chuang, L.T., Strnad, M., 2003a. Changes in sugars, organic acids and amino acids in medlar (*Mespilus germanica* L.) during fruit development and maturation. *Food Chem.* 83, 363–369.
- Glew, R.H., Ayaz, F.A., Sanz, C., Vanderjagt, D.J., Huang, H.S., Chuang, L.T., Strnad, M., 2003b. Effect of postharvest period on sugars, organic acids and fatty acids composition in commercially sold medlar (*Mespilus germanica* 'Dutch') fruit. *Eur. Food Res. Technol.* 216, 390–394.
- Gruz, J., Ayaz, F.A., Torun, H., Strnad, M., 2011. Phenolic acid content and radical scavenging activity of extracts from medlar (*Mespilus germanica* L.) fruit at different stages of ripening. *Food Chem.* 124, 271–277.
- Gulcin, I., Topal, F., Sarıkaya, S.B.O., Bursal, E., Bilsel, G., Gören, A.C., 2011. Polyphenol contents and antioxidant properties of medlar (*Mespilus germanica* L.). *Rec. Nat. Prod.* 5, 158–175.
- Gutierrez, M.S., Trinchero, G.D., Cerri, A.M., Vilella, F., Sozzi, G.O., 2008. Different responses of goldenberry fruit treated at four maturity stages with the ethylene antagonist 1-methylcyclopropene. *Postharvest Biol. Technol.* 48, 199–205.
- Hagerman, A.E., Riedl, K.M., Jones, G.A., Sovik, K.N., Ritchard, N.T., Hartzfeld, P.W., Riechel, T.L., 1998. High molecular weight plant polyphenolics (tannins) as biological antioxidants. *J. Agric. Food Chem.* 46, 1887–1892.
- Hertog, M.G.L., Feskens, E.J.M., Hollman, P.C.H., Katan, M.B., Kromhout, D., 1993. Dietary antioxidant flavonoids and risk of coronary heart-diseases – the Zutphen Elderly study. *Lancet* 342, 1007–1011.
- Hoang, N.T.T., Golding, J.B., Wilkes, M.A., 2011. The effect of postharvest 1-MCP treatment and storage atmosphere on 'Cripps Pink' apple phenolics and antioxidant activity. *Food Chem.* 127, 1249–1256.
- Itai, A., Tanahashi, T., 2008. Inhibition of sucrose loss during cold storage in Japanese pear (*Pyrus pyrifolia* Nakai) by 1-MCP. *Postharvest Biol. Technol.* 48, 355–363.
- Jeong, H., Huber, D.J., Sargent, S.A., 2003. Delay of avocado (*Persea americana*) fruit ripening by 1-methylcyclopropene and wax treatments. *Postharvest Biol. Technol.* 28, 247–257.
- Karhan, M., Aksu, M., Tetik, N., Turhan, I., 2004. Kinetic modelling of anaerobic thermal degradation of ascorbic acid in Rose Hip (*Rosa canina* L.) pulp. *J. Food Qual.* 27, 311–319.
- Kays, S.J., 1991. Metabolic process in harvested products-respiration. In: *Post Harvest Physiology of Perishable Plant Products*. Van Nostrand Reinhold Publication, New York, pp. 75–79.
- Khanbabaee, K., Ree, T.V., 2001. Tannins: classification and definition. *Nat. Prod. Rep.* 18, 641–649.
- Li, C., Shen, W., Lu, W., Jiang, Y., Xie, J., Chen, J., 2009. 1-CP delayed softening and affected expression of XET and EXP genes in harvested cherimoya fruit. *Postharvest Biol. Technol.* 52, 254–259.
- Li, F., Zhang, X., Song, B., Li, J., Shang, Z., Guan, J., 2013. Combined effects of 1-MCP and MAP on the fruit quality of pear (*Pyrus bretschneideri* Reld cv. Laiyang) during cold storage. *Sci. Hort.* 164, 544–551.
- Lohani, S., Prabodh, K., Pravendra, H., 2004. Changes in activities of cell wall hydrolases during ethylene-induced ripening in banana: effect of 1-MCP, ABA and IAA. *Postharvest Biol. Technol.* 21, 119–126.
- Maftoonzad, N., Ramaswamy, H.S., Marcotte, M., 2008. Shelf-life extension of peaches through sodium alginate and methyl cellulose edible coatings. *Int. J. Food Sci. Technol.* 43, 951–957.
- Mahajan, B.V.C., Singh, K., Dhillon, W.S., 2010. Effect of 1-methylcyclopropene (1-MCP) on storage life and quality of pear fruits. *J. Food Sci. Technol.* 47, 351–354.
- Maisuthisakul, P., Suttajit, M., Pongsawatmanit, R., 2007. Assessment of phenolic content and free radical-scavenging capacity of some Thai indigenous plants. *Food Chem.* 100, 1409–1418.
- Mao, L., Wang, G., Que, F., 2007. Application of 1-methylcyclopropene prior to cutting reduces wound responses and maintains quality in cut kiwifruit. *J. Food Eng.* 78, 361–365.
- Mayer, A.M., Harel, E., 1979. Polyphenol oxidases in plants. *Phytochemistry* 18, 193–215.
- McGuire, R.G., 1992. Reporting of objective colour measurements. *HortScience* 27, 1254–1255.
- Minas, I.S., Crisosto, G.M., Holcroft, D., Vasilakakis, M., Crisosto, C.H., 2013. Postharvest handling of plums (*Prunus salicina* Lindl.) at 10 °C to save energy and preserve fruit quality using an innovative application system of 1-MCP. *Postharvest Biol. Technol.* 76, 1–9.
- Nabavi, S.F., Nabavi, S.M., Ebrahimzadeh, M.A., Asgarirad, H., 2011. The antioxidant activity of wild medlar (*Mespilus germanica* L.) fruit, stem bark and leaf. *Afr. J. Biotech.* 10, 283–289.
- Piriyavinit, P., Ketsa, S., van Doorn, W.G., 2011. 1-MCP extends the storage and shelf life of mangosteen (*Garcinia mangostana* L.) fruit. *Postharvest Biol. Technol.* 6, 15–20.
- Romero-Rodriguez, A., Simal-Lozano, J., Vazquez-Oderiz, L., Lopez-Hernandez, J., Gonzalez-Castro, M.J., 2000. Physical, physicochemical and chemical changes during maturation of medlars and persimmons. *Dtsch. Lebensm. Rundsch.* 96, 142–145.
- Rop, O., Sochor, J., Jurikova, T., Zitka, O., Skutkova, H., Mlcek, J., Salas, P., Kraska, B., Babula, P., Adam, V., Kramarova, D., Beklova, M., Provaznik, I., Kizek, R., 2011. Effect of five different stages of ripening on chemical compounds in medlar (*Mespilus germanica* L.). *Molecules* 16, 74–91.
- Salvador, A., Arnal, L., Monterde, A., Cuquerella, J., 2004. Reduction of chilling injury symptoms in persimmon fruit cv. 'Rojo Brillante' by 1-MCP. *Postharvest Biol. Technol.* 33, 285–291.
- Selcuk, N., Erkan, M., 2015. The effects of modified and palliflex controlled atmosphere storage on postharvest quality and composition of 'Istanbul' medlar fruit. *Postharvest Biol. Technol.* 99, 9–19.
- Singh, S.P., Pal, R.K., 2008. Response of climacteric-type guava (*Psidium guajava* L.) to postharvest treatment with 1-MCP. *Postharvest Biol. Technol.* 47, 307–314.
- Singh, S.P., Singh, Z., 2012. Postharvest oxidative behaviour of 1-methylcyclopropene treated Japanese plums (*Prunus salicina* Lindell) during storage under controlled and modified atmospheres. *Postharvest Biol. Technol.* 74, 26–35.
- Sisler, E.C., M. Serek, M., 1997. Inhibitors of ethylene responses in plants at the receptor level: recent developments. *Physiol. Plant.* 100, 577–582.
- Sivakumar, S., Korsten, L., 2010. Fruit quality and physiological responses of litchi cultivar McLean's Red to 1-methylcyclopropene pre-treatment and controlled atmosphere storage conditions. *LWT Food Sci. Technol.* 43, 942–948.
- Spanos, G.A., Wrolstad, R.E., 1990. Influence of processing and storage on the phenolic composition of Thompson Seedless Grape juice. *J. Agric. Food Chem.* 38, 1565–1571.
- Sun, B., Yan, H., Liu, N., Wei, J., Wang, Q., 2012. Effect of 1-MCP treatment on postharvest quality characters, antioxidants and glucosinolates of Chinese kale. *Food Chem.* 131, 519–526.
- Tucker, G.A., 1993. Introduction. In: Seymour, et al. (Eds.), *Biochemistry of Fruit Ripening*. Chapman & Hall, London, UK, pp. 9–10.
- Valdenegro, M., Fuentes, L., Herrera, R., Moya-León, M.A., 2012. Changes in antioxidant capacity during development and ripening of goldenberry (*Physalis peruviana* L.) fruit and in response to 1-methylcyclopropene treatment. *Postharvest Biol. Technol.* 67, 110–117.
- Vinson, J.A., Jang, J., Dabbagh, Y.A., Serry, M.M., Cai, S., 1995. Plant polyphenols exhibit lipoprotein-bound antioxidant activity using an in vitro oxidation model heartdisease. *J. Agric. Food Chem.* 43, 2798–2799.
- Watkins, C.B., 2006. The use of 1-methylcyclopropene (1-MCP) on fruits and vegetables. *Biotechnol. Adv.* 24, 389–409.

- Watkins, C.B., Nock, J.F., Whitaker, B.D., 2000. Responses of early, mid and late season apple cultivars to postharvest application of 1-methylcyclopropene (1-MCP) under air and controlled atmosphere storage conditions. *Postharvest Biol. Technol.* 19, 17–32.
- Yang, H., Zhou, C., Wu, F., Cheng, J., 2010. Effect of nitric oxide on browning and lignification of peeled bamboo shoots. *Postharvest Biol. Technol.* 57, 72–76.
- Zhang, Z., Huber, D.J., Rao, J., 2011. Ripening delay of mid-climacteric avocado fruit in response to elevated doses of 1-methylcyclopropene and hypoxia-mediated reduction in internal ethylene concentration. *Postharvest Biol. Technol.* 60, 83–91.
- Zhang, Z., Tian, S., Zhu, Z., Xu, Y., Qin, G., 2012. Effects of 1-methylcyclopropene (1-MCP) on ripening and resistance of jujube (*Zizyphus jujuba* cv. Huping) fruit against postharvest disease. *LWT Food Sci. Technol.* 45, 13–19.
- Zheng, Y., Wang, C.Y., Wang, S.Y., Zheng, W., 2003. Effect of high-oxygen atmospheres on blueberry phenolic, anthocyanins, and antioxidant capacity. *J. Agric. Food Chem.* 51, 7162–7169.